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NITROGEN CYCLING IN APHOTIC COASTAL SANDY SEDIMENTS OF THE BALTIC SEA

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NITROGEN CYCLING IN APHOTIC COASTAL SANDY SEDIMENTS OF THE BALTIC SEA

DANA HELLEMANN

ACADEMIC DISSERTATION

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Nitrogen cycling in aphotic coastal sandy sediments of the Baltic Sea

Dana Hellemann

Ecosystems and Environment Research Programme, Faculty of Biological and Environmental Sciences, University of Helsinki, Finland; Academic Dissertation

Benthic nitrogen (N) cycling in sandy sediments in the stratified aphotic coastal zone (> 15 m) of the Baltic Sea was investigated along a north–south environmental gradient of N loading, trophic status, coastal geomorphology and sediment permeability. The aim was to establish a more comprehensive view of the Baltic Sea coastal N filter, where N transformation processes remove (via denitrification and anaerobic ammonium oxidation) and retain (via dissimilatory nitrate reduction to ammonium) land-derived N and thereby reduce its availability to the open sea; so far these processes have not been quantified in the deeper, aphotic sandy sediments. The main results are that a) not all sandy sediments were permeable enough to experience advective pore-water flow – mass transport in non-permeable sands functions via diffusion and fauna-mediated fluxes only, which simplifies biogeochemical measurement design; b) N removal rates were affected by the availability of labile particulate organic matter as a source of labile organic carbon and N, resulting in higher removal rates in eutrophic than in oligotrophic conditions, as well as similar removal rates in non-permeable sands and muds when also the substrate availability was similar; c) seasonal N removal in the stratified aphotic coastal zone is largely driven by the hydrography-controlled development of bottom water temperature, and differs from the seasonal pattern observed in the mixed photic coastal zone; and d) the role of dissimilatory nitrate reduction to ammonium in the aphotic coastal sandy sediments of the Baltic Sea is presumably more important than previously anticipated. These results indicate that the sandy sediments in the aphotic coastal zone of the Baltic Sea have an important role in N removal and retention, and are thus an integral component of the Baltic coastal N filter. The results further show the strong influence of the local environment on N cycling rates, emphasizing the need for context dependent data analysis, particularly in a diverse coastal setting such as in the Baltic Sea.

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Original publications and author's contribution

I **Hellemann D**, Tallberg P, Bartl I, Voss M & Hietanen S (2017) Denitrification in an oligotrophic estuary: a delayed sink for riverine nitrate. *Marine Ecology Progress Series* 583: 63-80.

DH designed the study together with PT and SH, and did the field sampling with contributions from PT. DH did the basic laboratory analysis and the data analysis with contributions from SH. DH was responsible for manuscript preparation with contributions from PT, IB, MV and SH.

II Bartl I, **Hellemann D**, Rabouille C, Schulz K, Tallberg P, Hietanen S & Voss M (2018) Particulate organic matter controls benthic microbial N-retention and N-removal in contrasting estuaries of the Baltic Sea. *Biogeosciences Discussions*.

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III **Hellemann D**, Tallberg P, Aalto SL, Bartoli M & Hietanen S. Seasonal cycle of benthic denitrification and DNRA in the aphotic coastal zone, northern Baltic Sea. Submitted to *Marine Ecology Progress Series*.

DH designed the study together with PT and SH. DH did the field sampling, basic laboratory analysis and the data analysis. SLA did the laboratory analyses of nitrogen gas production. DH was responsible for manuscript preparation with contributions from PT, MB, SLA and SH.

CR = Christophe Rabouille, DH = Dana Hellemann, IB = Ines Bartl, KS = Kirstin Schulz, MB = Marco Bartoli, MV = Maren Voss, PT = Petra Tallberg, SLA = Sanni L. Aalto, SH = Susanna Hietanen

Abbreviations

Anammox	Anaerobic ammonium oxidation
Ar	Argon
BBL	Benthic boundary layer
DIN	Dissolved inorganic nitrogen (sum of nitrite, nitrate and ammonium)
Dn	Denitrification of nitrate originating from nitrification in the sediment
DNRA	Dissimilatory nitrate reduction to ammonium
DNRAn	DNRA using nitrate originating from nitrification in the sediment
DNRAw	DNRA using nitrate originating from the bottom water
DOM	Dissolved organic matter
Dw	Denitrification of nitrate originating from the bottom water
D14	Denitrification rate of unlabelled nitrate
D15	Denitrification rate of isotopically labelled nitrate
IPT	Isotope pairing technique
LOI	Loss on ignition
^{15}N	Stable nitrogen isotope ('heavy nitrogen')
$^{15}N\text{-}NO_3^-$	Isotopically labelled nitrate
N	Nitrogen
N_2	Dinitrogen
N_2O	Nitrous oxide
NH_4^+	Ammonium
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
OPD	Oxygen penetration depth
POM	Particulate organic matter
TN	Total nitrogen

1 Introduction

The coastal zone at the interface between land and sea plays an integral role in the turnover of land-derived nutrient and organic matter loads on their way to the open sea. Its shallow water depth enables a tight benthic–pelagic coupling (Middelburg & Soetaert 2004) that connects the elemental cycles of sediment and water column, linking benthic organic matter mineralization to pelagic organic matter production. Thereby, land-derived loading is either temporally retained or permanently removed within the coastal zone, leading to the concept of a 'coastal filter' (Billen et al. 1991, Asmala et al. 2017).

Nitrogen (N) is one of the main elements of land-derived nutrient loading to coastal waters worldwide (Howarth et al. 1996). Extensive anthropogenic additions of biologically reactive N to the environment, particularly by agriculture and the combustion of fossil fuels (Galloway & Cowling 2002, Rabalais 2002), have strongly increased its availability in naturally N-limited coastal waters (Ryther & Dunstan 1971), resulting in widespread coastal eutrophication (Rosenberg 1985, Nixon 1995, Howarth & Marino 2006). Eutrophication is defined as an increase in the rate of organic matter supply to a system, for instance due to autochthonous production based on high nutrient availability (Nixon 1995). Ecosystem effects of eutrophication can be severe, ranging from oxygen deficiency of bottom waters to loss of biodiversity (Smetacek et al. 1991, Rabalais 2002, Diaz & Rosenberg 2008), which can also affect the N retention and removal processes of the coastal filter (Jäntti & Hietanen 2012).

N retention processes transform biologically reactive N temporarily to different chemical N forms, while keeping it bioavailable (Asmala et al. 2017). Processes include the uptake of dissolved inorganic nitrogen (DIN, sum of nitrate [NO_3^-], nitrite [NO_2^-] and ammonium [NH_4^+]) in primary production and its subsequent transfer to the organic N pool, mineralization of organic N back to DIN via ammonification and nitrification, and the transformation of NO_3^- to NH_4^+ via dissimilatory nitrate reduction to ammonium (DNRA).
N removal processes remove biologically reactive N permanently from the reach of biological utilization within a system (Asmala et al. 2017) and thereby have the potential to mitigate eutrophication. The processes are N burial and the production of gaseous N forms in denitrification (dinitrogen [N_2], nitrous oxide [N_2O]) and anaerobic ammonium oxidation (anammox; N_2). The only exception to N_2 production being a N removal pathway is N_2 fixation, which can transform the generally biologically unreactive N_2 to NH_4^+, adding it back to the system. N retention and removal processes are linked by the exchange of products, particularly NH_4^+ and

NO_3^-, which happens mainly in the sediment and forms the benthic N cycling[1] (Figure 1).

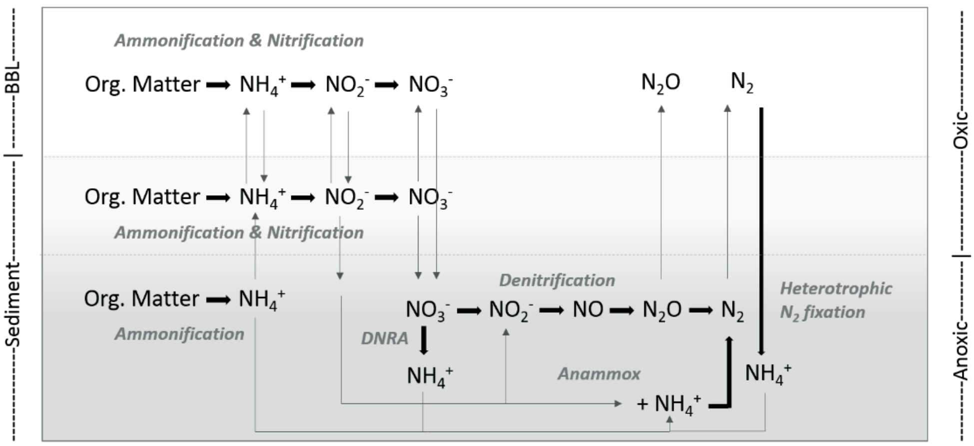

Figure 1: Main processes of benthic nitrogen (N) cycling shown for an aphotic sediment (i.e. excluding benthic primary production), with anammox = anaerobic ammonium oxidation, BBL = benthic boundary layer (i.e. the turbulent water layer directly above the sediment, Richards 1990), DNRA = dissimilatory nitrate reduction to ammonium, N_2 = dinitrogen, N_2O = nitrous oxide, NH_4^+ = ammonium, NO = nitric oxide, NO_2^- = nitrite, NO_3^- = nitrate, org. matter = organic matter. Thick black arrows indicate reaction steps, whereas thin grey arrows indicate diffusion pathways. The sediment surface and oxic–anoxic interface are shown as dashed lines for illustration purposes.

Ammonification transforms the organic N contained in organic matter to NH_4^+, which under oxic conditions is subsequently stepwise oxidized to NO_2^- and NO_3^- during nitrification. All end products of the single reactions (NH_4^+, NO_2^- and NO_3^-) diffuse between the BBL and oxic sediment, as well as between the oxic and anoxic sediment depending on the concentration gradients. That means that NO_2^- and NO_3^- mainly diffuse from the oxic to the anoxic environment, as they are produced in oxic and consumed in anoxic conditions. In contrast, NH_4^+ mainly diffuses from the anoxic to the oxic environment, as the accumulation of produced NH_4^+ is usually larger in the anoxic than in the oxic environment, where it can be rather quickly consumed during nitrification. In the anoxic sediment below the oxic–anoxic interface, NO_3^- from the BBL or from the oxic sediment layer is stepwise reduced to N_2O and N_2 during denitrification or directly reduced to NH_4^+ during DNRA. NO_2^- from the oxic sediment layer is also denitrified or taken up together with NH_4^+ to form N_2 in anammox. N_2 is the main gaseous end product in both denitrification and anammox; high amounts of N_2O can be released from denitrification under disturbed environmental conditions, such as high organic loading (Seitzinger & Nixon 1985). N_2 from the BBL can be fixed to NH_4^+ in benthic heterotrophic N_2 fixation (Fulweiler et al. 2007, Newell et al. 2016).

[1] I refer to it as *cycling* as it is not a closed cycle but merely the benthic part of the entire N cycle that includes sediment, water column and atmosphere.

Sediments are particularly suitable habitats for N cycling. They provide organic carbon from organic matter mineralization, which is used as an electron donor in heterotrophic N transformation processes such as denitrification, as well as oxic and anoxic reaction zones for the aerobic and anaerobic N transformation processes, which are linked by the exchange of end products across the oxic–anoxic interface (Figure 1). The tight connection of aerobic and anaerobic processes renders benthic N cycling sensitive to the sediment oxygen content and the outline of the oxic–anoxic interface.

In fine-grained, cohesive sediments, where solutes are transported by molecular diffusion along concentration gradients and by fauna-mediated fluxes, the oxic–anoxic interface is generally two-dimensional (2D) horizontal, with vertical exceptions for example around faunal burrows (Aller 2014). N cycling in cohesive sediments has been well-studied worldwide (Devol 2015), as most measurement methods are suitable for diffusive solute supply and a horizontal oxic–anoxic interface. For instance, the classic application of the isotope pairing technique (IPT; Nielsen 1992) for measuring denitrification rates is a diffusive core incubation of sediment with a 2D redox zonation, as the technique requires a homogeneous supply and uptake of the isotopic tracer to make the mathematical quantification of process rates from measured rates of tracer processing possible.

In coarse-grained, permeable sediments such as well-sorted sands, advective pore-water flow adds to diffusive and fauna-mediated transport processes. Horizontal pressure gradients at the sediment surface, such as those created by the interaction of bottom flow with bottom topography (Huettel & Gust 1992a) or by the influence of waves (Riedl et al. 1972, McLachlan & Turner 1994), push near-bottom water into and pore-water out of the permeable pore space. Thereby, entire water parcels with dissolved and suspended matter are transported quickly into, through and out of the sediment (Webb & Theodor 1968, Thibodeaux & Boyle 1987, Huettel & Gust 1992b, Huettel et al. 2003, 2014), resulting in a complex, three-dimensional oxic–anoxic interface shaped by the flow path (Huettel et al. 1998, Precht et al. 2004) and high elemental turnover (Boudreau et al. 2001).

As the pressure gradients at the sediment surface are determined by the local conditions of water energy and bottom topography, advective pore-water flow is highly variable in space and time (Janssen et al. 2005a), which makes permeable sediments a 'non-deterministic environment' (Cardenas et al. 2008) and the measurement of N transformation processes a methodological challenge (Huettel et al. 2014). For instance, equipment deposited at the sediment surface for *in situ* measurements changes the bottom flow and consequently the pressure gradients and the pore-water flow (Huettel & Gust 1992b), while sediment sampling for *ex situ* measurements stops the pore-water flow, pore-water can be lost altogether (Janssen et al. 2005a), and the artificial reconstruction of the pore-water flow pattern and velocity is mostly a generalized approximation of the complex *in situ* conditions.

The incubation design used to represent advective conditions during N process measurements includes whole core percolations (Rao et al. 2007, 2008, Evrard et al. 2013, Marchant et al. 2014, 2016), core percolations to the depth of the advective layer (Gao et al. 2010, 2012, Gihring et al. 2010), stirred chambers that induce pore-water flow through radial pressure gradients (Cook et al. 2006, Gihring et al. 2010) and flume tanks (Huettel et al. 1998, Kessler et al. 2012, 2013). The denitrification rates obtained in these measurements indicate the complexity of N cycling in permeable sands, with process rates ranging from < 1 to > 5000 µmol N m^{-2} d^{-1} and disparity regarding the main source of the denitrified NO_3^-. For instance, on the one hand, pore-water flow has been shown to stimulate nitrification by increasing the oxic sediment volume (Huettel et al. 1998, Gihring et al. 2010, Marchant et al. 2016), to enhance the areal oxic–anoxic interface across which NO_3^- and NH_4^+ can be exchanged (Precht et al. 2004, Cook et al. 2006) and hence to favour denitrification coupled to NO_3^- produced in the sediment (Dn; Rao et al. 2008, Marchant et al. 2016). Yet, on the other hand, pore-water flow has also been shown to separate the oxic inflow from the anoxic outflow zone, limiting the exchange of NO_3^- and NH_4^+ across the oxic–anoxic interface (Huettel et al. 1998, Cook et al. 2006, Kessler et al. 2012, 2013), and thus to favour denitrification of NO_3^- from the bottom water (Dw; Cook et al. 2006, Kessler et al. 2012, 2013, Marchant et al. 2014).

However, not all sandy sediments experience advective pore-water flow with significant effects on sediment biogeochemistry as just described (Forster et al. 2003, Janssen et al. 2005b). Following Darcy's Law (Darcy 1856), the velocity of pore-water flow is proportional to sediment permeability and pressure gradients at the sediment surface. Hence, low permeability and low pressure gradients can decrease the flow velocity until its effects on sediment biogeochemistry are not distinguishable from the effects of molecular diffusion (Glud et al. 1996). This is the threshold for the onset of significant advective pore-water flow in the sediment, estimated to occur at a Peclet number ≥ 5 (ratio of advective to diffusive velocity; Bear 1972). Water energy is the common factor affecting both sediment permeability and the magnitude of pressure gradients (Huettel et al. 2003). High water energy creates well-sorted, coarse-grained, clean sediments with large open pore spaces (McLachlan & Turner 1994), whose weak cohesive forces enable pore-water flow in response to pressure gradients. At lower water energy, sediments are less well-sorted and accumulate more material (McLachlan & Turner 1994, Forster et al. 2003), which reduces the open pore space and increases the cohesive forces onto the pore-water. To move pore-water in such sediments of lower permeability, pressure gradients need to be correspondingly higher (Janssen et al. 2005b), but they too depend on the local water energy. This makes advective pore-water flow less likely in sands of low energy environments, such as the semi-enclosed Baltic Sea.

About 21% of the Baltic Sea floor is covered by sandy sediments, mainly in the western and southern open areas and along the southern and south-eastern coastal zone, where they were deposited during the last glaciation. Only a few larger sandy areas can be found in the northern parts (southern and western Finnish coast, northern Bothnian Bay; Al-Hamdani & Reker 2007). The water energy at the Baltic coast is lower than in most shelf systems due to the absence of significant tides (< 19 cm tidal oscillation; Medvedev et al. 2013) and low average bottom current velocity (0–2 cm s^{-1}; Al-Hamdani & Reker 2007). Owing to the low water energy, a sediment permeability of ≥ 2.5 × 10^{-12} m^2 has been defined as the threshold for the onset of advective pore-water flow with significant effects on sediment biogeochemistry in Baltic Sea sands (Forster et al. 2003). In comparison, in systems of higher water energy, the effects of advective pore-water flow can already be expected at a sediment permeability of ≥ 1.0 × 10^{-12} m^2 (Huettel et al. 2003).

The Baltic Sea coastal zone receives annually ~ 680 kt riverine total nitrogen (TN, average 1994–2014; HELCOM 2015, 2018), of which the southern sandy coast receives the main share delivered by the rivers Oder, Vistula, Neman and Daugava (Stålnacke et al. 1999). In a modelling study, this riverine N has been estimated to stay only a maximum of 1.4 years within the coastal zone before disappearing (Radtke et al. 2012). This result matched local nutrient concentrations and natural abundances of stable N isotopes (Voss et al. 2005, Korth et al. 2013), which indicated that a substantial part of the riverine N load must be removed in the southern Baltic sandy sediments, for instance via advection-driven high N turnover as observed at other sandy coasts (e.g. North Sea: Gao et al. 2012, Marchant et al. 2014, 2016). However, large parts of the southern Baltic sandy sediments have been estimated to be poorly sorted, likely as a result of high particle residence time and limited winnowing events due to low water energy; only ~ 80% of the well-sorted sands likely experience advective pore-water flow (sediments > 10 m depth, permeability threshold ≥ 2.5 × 10^{-12} m^2; Forster et al. 2003). This indicates that conclusions about N cycling derived from highly permeable sands of high energy environments, such as the North Sea, cannot simply be applied to the less permeable sandy sediments of the Baltic Sea.

A further distinct difference between the Baltic Sea and other coastal seas is its highly diverse environment with varying coastal geomorphology and strong spatial gradients in N load and composition, as well as salinity, humic substances and species composition (the three last factors are, however, not discussed in this thesis, as I did not observe effects on benthic N cycling). The northern Baltic coast is rugged with dense archipelagos, while the southern coast is smoothly stretched with large bays, lagoons and estuaries (Al-Hamdani & Reker 2007; Figure 2). N loading increases in total amount and DIN percentage from north to south in response to increasing anthropogenic pressures in the catchment area (Stålnacke et al. 1999, Stepanauskas et al. 2002, HELCOM 2018), which changes from sparsely populated boreal forests in the north to agriculture and urbanization in the south (Sweitzer et al. 1996). Different N loading and geomorphology along the coast can affect benthic N cycling, for example, by influencing the local availability and residence time of N species and organic matter (Seitzinger et al. 2006).

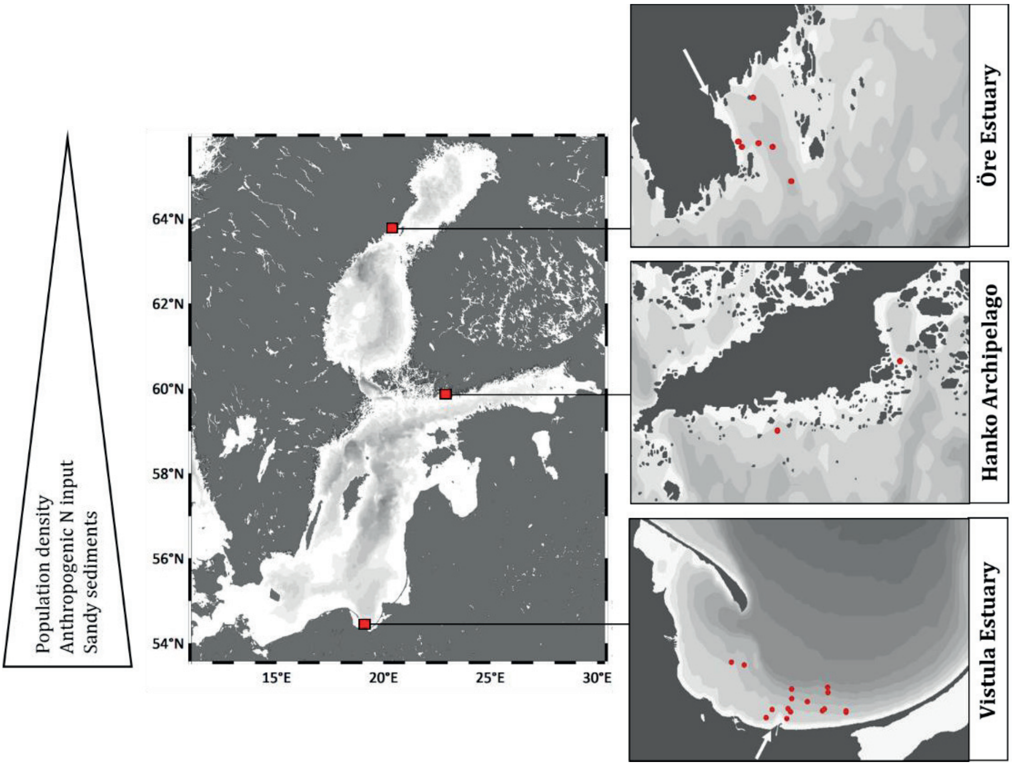

Figure 2: Symbolic gradient of major environmental parameters that likely affect coastal benthic nitrogen (N) cycling along the north–south extension of the Baltic Sea, and sampling sites along this gradient with a detailed view of every site. Sampled stations at each site are pooled from all campaigns (Table 1) and are shown as red dots. The river mouths in the estuarine sites are indicated by white arrows, and bottom bathymetry is shown in grey shades. The figure was drawn using Ocean Data View (Schlitzer 2015). Please note: while being a major parameter of the Baltic Sea environment, the north–south salinity gradient is not shown, as the data did not indicate an effect of salinity on benthic N cycling.

2 Objectives

Actual measurements of N removal and N retention processes in Baltic Sea sandy sediments are scarce. The few measurements available are from the shallow, photic, mixed coastal zone and are obtained without accounting for potential advective pore-water flow where necessary (Nielsen et al. 1995, Sundbäck et al. 2006, Deutsch et al. 2010, Zilius et al. 2018). This leaves out the deeper, aphotic, seasonally-stratified coastal zone and representative measurements of N turnover in permeable sands, particularly at the southern coast. In consequence, we currently lack a basic understanding of N cycling in Baltic coastal sands and therefore also a comprehensive understanding of functioning and efficiency of the Baltic coastal N filter, of which sandy sediments are an integral part.

Therefore, I studied benthic N cycling in sandy sediments of three coastal sites along the described north–south environmental gradient in the Baltic Sea, including two estuaries and one archipelago site (Figure 2). All sites were aphotic and located below the mixed surface layer depth (> 10 m, Leppäranta & Myrberg 2009; Table 1) thus representing the aphotic and seasonally density-stratified part of the coastal zone. In detail, this thesis aims to answer the following questions:

- What are the sediment characteristics of the studied Baltic sands in terms of sediment permeability and mass transport, and how does sediment permeability change along the aphotic coastal zone?
- What are the implications of non-permeable sandy sediments for biogeochemical measurement design and benthic N cycling?
- How much N is removed in the permeable sandy sediments of the southern Baltic coast, and do the measured rates relate to the suggested high N removal in these sands (Voss et al. 2005, Korth et al. 2013)? How do N removal rates in permeable sands of the Baltic Sea compare with N removal rates in permeable sands of systems with higher water energy, e.g. the North Sea?
- How do the diverse environmental conditions of the Baltic Sea (coastal geomorphology, N loading, trophic status, sediment composition) affect coastal N removal rates from north to south? What is the key environmental factor influencing N removal rates?
- Does N cycling in the stratified, aphotic coastal zone follow the same seasonality in both sandy and muddy sediments, and does the seasonality differ from observations in the photic, mixed coastal zone? What is the key environmental factor influencing seasonal N cycling?
- What is the role of DNRA in aphotic coastal sandy sediments of the Baltic Sea, where so far process quantifications have been neglected?
- What are the implications for our current understanding of the aphotic coastal N filter in the Baltic Sea when including the obtained results on sandy sediment?

These objectives are integrated in the following three papers:

Paper I focuses on N removal in one of the very few oligotrophic estuaries on the Baltic coast (Öre Estuary; HELCOM 2014) and introduces the concept of non-permeable sandy sediments without significant advective pore-water flow. Estuaries in the Baltic Sea receive the annually highest riverine TN load in spring due to the snow melt; this paper analyses the fate of this spring N load within the estuary and estimates how efficiently the oligotrophic estuary functions as a N filter.

Paper II focuses on the impact of different environments on the efficiency of estuaries as N filters. N removal rates from the oligotrophic estuary of paper I are compared with rates from a eutrophic estuary (Vistula Estuary). Both estuaries furthermore differ in riverine N load, sand permeability (permeable vs non-permeable), size, geomorphology and particle residence time. The paper identifies key environmental factors controlling benthic N cycling in these estuaries and discusses the role of the southern Baltic permeable sands in coastal N removal.

Paper III focuses on the seasonal cycle of N removal (denitrification, anammox) and N retention (DNRA) in sandy and muddy sediments of the aphotic, stratified coastal zone, and whether the seasonal pattern differs between sediment types and in comparison to the photic, mixed coastal zone. The study sites are located at an archipelago coast (Hanko Archipelago), where organic-poor sandy transportation bottoms can be found in close proximity to organic rich muddy accumulation sites. The seasonal study adds further evidence to the identification of key environmental factors for N cycling in coastal Baltic sandy sediments.

3 Materials and Methods

3.1 Study sites

The oligotrophic *Öre Estuary* on the Swedish coast of the Quark Strait between the Bothnian Bay and the Bothnian Sea is a small (~ 1 km^3, SMHI 2003), semi-enclosed estuary with fine-grained sandy and 'muddy' sediments (i.e. grain size < 63 µm). The inner part of the estuary deepens into a small trough that rises again at the estuary mouth, creating a natural topography threshold (Brydsten 1992) and resulting in a particle residence time of ≥ 1 year (Brydsten & Jansson 1989). The eutrophic *Hanko Archipelago* on the Finnish coast of the Gulf of Finland comprises exposed sandy transportation bottoms and more sheltered muddy accumulation basins. The eutrophic *Vistula Estuary* on the Polish coast of the Bay of Gdansk is a large (~ 20 km^3, paper II), open estuary with very fine- to coarse-grained sandy sediments. Particle residence time is likely short, as bottom waters can merge freely with the adjacent coastal and offshore waters. The water column at all three sites was oxic and seasonally density stratified; all studied sediments were aphotic.

3.2 Field sampling

Samples were collected from 2014 to 2016 (Table 1). The estuaries were sampled at high (spring) and low (summer) river outflow and N loading onboard RV *Lotty* (Umeå Marine Sciences Centre; Öre Estuary) and RV *Elisabeth Mann Borgese* (Leibniz-Institute for Baltic Sea Research Warnemünde; Vistula Estuary). The archipelago site was sampled monthly during the ice-free period for one year using RV *Saduria* (University of Helsinki).

At each site, sampling followed the same routine. Water column hydrographic parameters (conductivity, temperature, depth and photosynthetically active radiation) were obtained before the sediments were sampled. If available, both sandy and muddy sediments were sampled (Öre Estuary, Hanko Archipelago). The sediment corers used were chosen depending on the sediment type (coarse to fine sand: Haps bottom corer; very fine sand to mud: Multi-Corer; mud: GEMINI/GEMAX twin corer). The Haps corer keeps pore-water of permeable sands within the sediment, as the core tube is closed tight with a rubber sealed top lid that creates a vacuum inside the tube (KC Denmark). From the first sediment core, the water overlying the sediment was sampled for the analysis of dissolved oxygen and N-nutrients (NO_2^-, NO_3^-, NH_4^+), followed by sediment sampling for the analysis of porosity, organic matter content via loss on ignition (LOI), grain size distribution and permeability (Table 2). Intact sediment cores were used in whole for pore-water concentration profiles of NH_4^+, and subsampled with acrylic core liners (inner diameter 2.3 cm) for pore-water concentration profiles of oxygen and measurements of N transformation processes. All samples were kept in the dark and at *in situ* temperature until processing in the laboratory (Table 2).

Table 1: Sampling details and corresponding publication of the studied Öre Estuary (ÖE), Hanko Archipelago (HA) and Vistula Estuary (VE). River discharge data: http://vattenwebb.smhi.se/station/ (Öre), Polish National Monitoring Programme of the Institute of Meteorology and Water Management's National Research Institute (Vistula). River total nitrogen (TN) data: calculated from own measurements per sampling months. DNRA = dissimilatory nitrate reduction to ammonium; n = number of sampled sites; N = nitrogen; N_2 = dinitrogen.

Site	Sampling period	n	Depth (m)	River discharge (m^3 s^{-1})	River TN load (t $month^{-1}$)	N processes measured	Paper
ÖE	20–24/04/15 03–07/08/15	8 8	15–37	66 26	98 26	Denitrification Anammox	I, II
HA	05–06/04/16 03–04/05/16 07–08/06/16 05–06/07/16 08–09/08/16 13–14/09/16 11–12/10/16 14–15/11/16	2 2 2 2 2 2 2 2	24, 33	–	–	Denitrification Anammox DNRA N_2 fixation[2]	III
VE	28/02–10/03/16 04–15/07/14	10 10	15–59	1 500 932	16 172 2 620	Denitrification Anammox	II

Table 2: Methods used for the analysis of bottom water, sediment and nitrogen (N) cycling parameters. Ar = argon; DNRA = dissimilatory nitrate reduction to ammonium; N_2 = dinitrogen; NH_4^+ = ammonium; NO_2^- = nitrite; NO_3^- = nitrate.

	Parameter	Method	References
Bottom water	Dissolved oxygen	Winkler iodometric titration	Winkler (1888)
	NO_2^-, NO_3^-, NH_4^+	Colorimetric determination	Grasshoff et al. (1983)
Sediment	Loss on ignition	Sediment weight loss in combustion (550°C, 4h)	Burdige (2006)
	Permeability	Constant head method for laminar flow of water through granular soil	Klute & Dirksen (1986)
	Pore-water NH_4^+	Rhizon™ sampling and colorimetric determination	Seeberg-Elverfeldt et al. (2005)
	Pore-water oxygen	Oxygen microelectrode profiling	Revsbech et al. (1980a)
	Porosity	Sediment weight loss in drying (105°C, overnight)	Burdige (2006)
	Sediment type	Classification based on grain size distribution obtained by wet sieving or laser particle size analysis	Wentworth (1922)
N cycling	Anammox	Revised isotope pairing technique	Risgaard-Petersen et al. (2003)
	Denitrification	Revised isotope pairing technique	Risgaard-Petersen et al. (2003)
	DNRA	Accumulation of isotopically labelled NH_4^+ during incubation with isotopically labelled NO_3^-	Christensen et al. (2000)
	N_2 fixation[2]	Negative N_2 flux measured via N_2/Ar ratio	Kana et al. (1994), Fulweiler et al. (2007)

[2]Benthic N_2 fixation was measured, but data are unpublished and not included in this thesis.

3.3 Incubation design of nitrogen cycling measurements

The incubation design used was chosen based on the sediment permeability and thus the likelihood of the presence (permeability $\geq 2.5 \times 10^{-12}$ m^2) or absence (permeability $< 2.5 \times 10^{-12}$ m^2) of pore-water flow with significant effects on sediment biogeochemistry (Forster et al. 2003). During the field campaigns, this decision was made based on an educated guess, as sediment permeability was measured later in the home laboratory. The analysis of oxygen profiles and oxygen penetration depth (OPD) in the sediments added decisive power, as pore-water flow can be seen in the sigmoidal shape of oxygen profiles (Revsbech et al. 1980b) and usually a large OPD based on the advective intrusion of oxic bottom water. However, as pore-water flow stops during sampling but oxygen consumption continues, oxygen profiles can also change quickly if oxygen consumption rates are high; hence, oxygen profiles cannot be used as the only parameter to identify pore-water flow.

The identification of mass transport and the decision for the incubation design were clear in all campaigns, except for the sandy sediments in the Vistula Estuary in summer 2014. These sands were assumed to be permeable but showed no sigmoidal oxygen profiles and a surprisingly shallow OPD (see Section 4.1; paper II). Hence, in that campaign, we used both a diffusive and an advective incubation design. The correct incubation method was verified later by analysing the hydrographic data and estimating a maximum *in situ* pore-water flow velocity and corresponding Peclet number during the sampling period (diffusion < Peclet number 5 < advection; Bear 1972, supplementary material of papers II and III). The same calculation was also used to verify the mass transport in the archipelago sand, whose permeability was close to the threshold for the onset of advection (paper III).

In the advective incubation (Figure 3A; Vistula Estuary), advective pore-water flow was mimicked by circulating pore-water through the advective sediment layer, which was estimated from the OPD following Gihring et al. (2010). Hence, the design is an advective layer percolation method similar to Gihring et al. (2010) and Gao et al. (2010), but with the main difference that the pore-water in this design was in motion during the whole incubation, not stagnant (detailed description: paper II). In the diffusive incubation (Figure 3B; Öre Estuary, Hanko Archipelago, Vistula Estuary summer), samples were incubated in gentle water motion representing diffusive conditions.

Independently of the incubation design, rates of denitrification, anammox and DNRA were measured based on microbial processing of isotopically labelled nitrate (^{15}N-NO_3^-, Nielsen 1992, Christensen et al. 2000, Risgaard-Petersen et al. 2003; detailed description: papers I–III, DNRA: paper III).

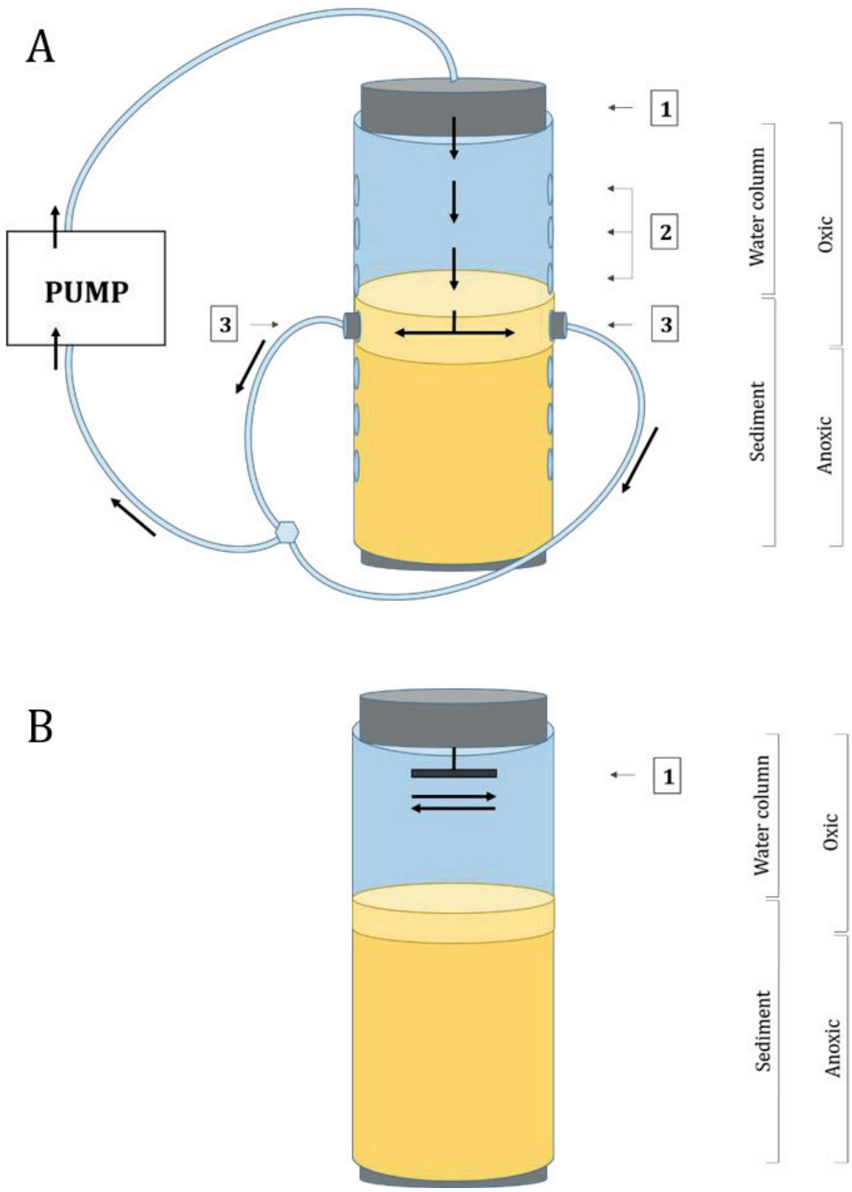

Figure 3: Incubation design used for measuring processes of benthic nitrogen cycling in permeable sediment under advective pore-water flow (A; paper II) and in non-permeable sediment under diffusive water motion (B; papers I–III). A: Bottom site water with isotopic tracer is pumped from the top into the water column of the incubation core (1) and drawn out again through the advective, oxic sediment layer (3), identified from the oxygen profiles. The outflow port can be adjusted (2), depending on the sediment height in the core and the depth of the advective layer. B: Isotopic tracer is added to the water column of the incubation core and thereafter distributed by diffusion, which is aided by gentle water motion from a magnetic stirrer (1).

4 Results and Discussion

4.1 Characteristics of sandy sediments in the aphotic coastal zone of the Baltic Sea

At the three studied sites, the sand types ranged from coarse sand in the southern Vistula Estuary to silty very fine sand in the northern Öre Estuary, with porosities in the typical range of sandy sediments and clearly different to muddy sediments (Table 3). Sediment permeability decreased from south to north and resulted in non-permeable sandy sediments without advective pore-water flow in the Hanko Archipelago and the Öre Estuary, likely due to the high share of very fine sand grains in the sand composition (papers I and III). Only sandy sediments in the Vistula Estuary were permeable enough to enable advective pore-water flow (Table 3), while this applied only to circa 56% of the estuarine sands (paper II). The remaining sands were non-permeable, probably due to accumulation of fine material as indicated by slightly higher LOI and porosity values compared with the permeable sands (Table 3).

Table 3: Sediment characteristics of the studied sites Öre Estuary (ÖE), Hanko Archipelago (HA) and Vistula Estuary (VE), pooled from all seasons as averages with standard deviation (potential seasonal effects are discussed in the respective papers). Porosity and loss on ignition (LOI, with dw = dry weight) from sediment depth 0–2 cm (sand) and 0–1 cm (mud), and ammonium (NH_4^+) pool from sediment depth 1–5 cm to indicate NH_4^+ accumulation. Sand of permeability $\geq 2.5 \times 10^{-12}$ m² is termed 'permeable' (p), and sand of permeability $< 2.5 \times 10^{-12}$ m² is termed 'non-permeable' (np). Number of replicates in brackets.

Site	Sediment classification (Wentworth 1922)	Porosity	LOI (dw %)	NH_4^+ pool (µmol m²)	Permeability (10^{-12} m²)
ÖE	Silty very fine / fine sand	0.61 ± 0.10 (7)	2.01 ± 0.83 (7)	984 ± 163 (5)	0.2 ± 0.1 (5) np
	'mud'	0.84 ± 0.10 (8)	8.40 ± 2.78 (8)	1512 ± 468 (7)	–
HA	Silty fine sand	0.45 ± 0.02 (8)	0.94 ± 0.10 (8)	1764 ± 458 (8)	2.0 ± 0.3 (7) np
	'mud'	0.94 ± 0.00 (7)	14.86 ± 0.87 (7)	5127 ± 2203 (6)	–
VE	Fine, medium, coarse sand	0.40 ± 0.05 (12)	0.85 ± 0.53 (12)	1182 ± 837 (7)	7.7 ± 5.6 (12) p
	Silty very fine sand, fine sand	0.63 ± 0.12 (8)	4.96 ± 3.46 (6)	4026 ± 3448 (5)	0.7 ± 0.2 (2) np

Advective pore-water flow in the permeable sands of the Vistula Estuary was visible in spring in the sigmoidal shape of the oxygen profiles, with nearly constant oxygen concentration in the top millimetres of sediment (Figure 4A, white triangles; Revsbech et al. 1980b), indicating continuous intrusion of oxic bottom water. In contrast, the oxygen profiles in the non-permeable sands of the Vistula Estuary in spring were parabolic shaped, indicating the absence of pore-water flow and that mass transport was mainly governed by diffusion (Figure 4A, black triangles; Revsbech et al. 1980b). In consequence, the OPD in spring was much larger in the permeable than in the non-permeable sand of the Vistula Estuary (Figure 4B).

Parabolic oxygen profiles in sandy sediments per se are not proof of the absence of advective pore-water flow, as high oxygen consumption can quickly distort an initial sigmoidal shape of the oxygen profile (Lohse et al. 1996). However, in combination with sediment permeability below the threshold for the onset of advection, it is very likely that parabolic oxygen profiles in non-permeable sandy sediments indicate a natural absence of advective pore-water flow. This was further supported by the oxygen profiles in sediments of the Öre Estuary and the Hanko Archipelago, which were nearly identical between non-permeable sandy and muddy sediments (Figure 4A).

In the Öre Estuary, the availability of labile organic matter was estimated to be similar between the sediment types (paper I), and hence the same mass transport mechanisms resulted in a similar OPD in sandy and muddy sediment (Figure 4B). The different LOI in the sediment types of the Öre Estuary do not contradict this conclusion, since LOI is a bulk measurement that does not differentiate between fresh labile and old refractory organic matter and therefore does not equal the amount of labile organic matter accessible for microbial utilization (Nedwell 1987).

In the Hanko Archipelago, the availability of labile organic matter was estimated to be much lower in the non-permeable sandy sediment than in the muddy sediment due to different coastal geomorphology (see Section 4.2.2). Consequently, a larger OPD based on lower organic matter respiration would have been expected in the sandy sediment compared with the muddy sediment; however, the OPD in summer was similar in both sediment types (Figure 4B). It is possible that in summer, when respiration was high, some oxygen was lost from the sandy samples, since measurements were made circa 2 hours after sampling owing to the long distance between sampling site and laboratory. Hence, the original OPD in the archipelago sandy sediments might indeed have been a bit larger.

Strikingly, during sampling in summer 2014, also the permeable sands of the Vistula Estuary showed parabolic oxygen profiles (Figure 4A, white circles) and an OPD similar to that of non-permeable sands of the same season (Figure 4B). At the same time, the permeable sands had higher sediment NH_4^+ pools compared with in spring (paper II), indicating NH_4^+ accumulation in a generally non-accumulating sediment type (Ehrenhauss et al. 2004). We discuss this finding extensively in paper II and suggest, that the bottom flow velocity at the time of sampling was too low (maximum 2.5 cm s^{-1}) to generate sufficient pressure gradients via interaction with bottom topography to trigger advective pore-water flow, despite high sediment permeability (Peclet number < 5; supplementary material of paper II). The observed very low bottom flow velocity likely originated from strong thermal stratification of the water column and is thus expected to be a temporary occurrence (paper II). To date, an absence of advective pore-water flow in permeable sands has been described in laboratory experiments (Glud et al. 1996, Ziebis et al. 1996) but to my knowledge not in nature.

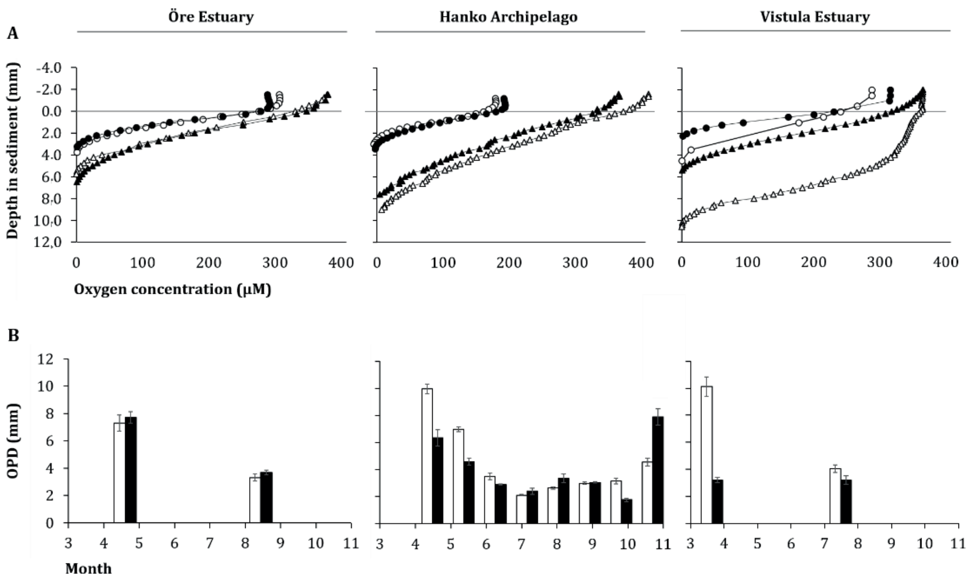

Figure 4: Example oxygen profiles (A) and average oxygen penetration depth (OPD) with standard deviation (B) in the sandy and muddy sediments of the studied sites. Data from sandy sediments are shown in white, and data from muddy sediments and the non-permeable sands in the Vistula Estuary are shown in black. Oxygen profiles are shown for spring (triangles) and summer (circles). The line at 0 mm indicates the sediment surface.

These results confirm that not all sandy sediments in the aphotic coastal zone of the Baltic Sea are permeable enough for advective pore-water flow, likely due to low sediment sorting from low water energy, in agreement with Forster et al. (2003). Mass transport in non-permeable sands and permeable sands temporarily without pore-water flow consequently functions via molecular diffusion and fauna-mediated fluxes as in cohesive, i.e. muddy, sediments. These results likely only apply to the deeper, stratified coastal zone of the Baltic Sea, as water energy increases with decreasing water depth (McLachlan & Turner 1994), potentially resulting in more permeable sands in the shallow, mixed coastal zone of the Baltic Sea.

Independent of sediment permeability, the organic matter content measured as LOI was generally low in all sandy sediments and was much lower than in the muddy sediments of the same location (Table 3). Low organic matter content in sandy sediment is usually associated with advection-driven high elemental turnover (Boudreau et al. 2001) which, however, can only explain the low LOI values of the permeable sands in the Vistula Estuary in spring. A further explanation for the low organic matter content in both permeable and non-permeable sandy sediments could be the generally low organic matter sorption capacity of sand grains based on a small surface to volume ratio (Mayer 1994, Hedges & Keil 1995). Additionally, also the particle residence time within an environment affects the organic matter content of sediment. This can be seen when comparing the LOI values from the sandy sediment in the Hanko Archipelago with estimated very short particle residence time

(Section 4.2.2; paper III) with the higher LOI values from the sandy sediments in the Öre Estuary with a particle residence time of ≥ 1 year (Brydsten 1992; Table 3).

4.2 Nitrogen cycling in sandy sediments in the aphotic coastal zone of the Baltic Sea

4.2.1 Suitability of applied incubation design

N transformation processes in sandy sediments that do not experience advective pore-water flow could be measured by using classic diffusive core incubations. This finding should simplify future work on N cycling in non-permeable sandy sediments, as diffusive incubations (including both core and benthic chamber incubations) are generally relatively easy to handle.

N transformation processes in sandy sediments that do experience advective pore-water flow were measured by using an incubation design with constant percolation of the advective layer. This was assumed to replicate *in situ* conditions by keeping the pore-water moving and only affecting the actual layer of *in situ* advective pore-water flow. However, despite using the lowest pump speed possible, the resulting pore-water flow velocity of ~ 7.6 cm h^{-1} was similar to pore-water flow velocities measured at high water energy (North Sea; Huettel et al. 1996, Precht et al. 2004) and was thus likely not representative of the calm Baltic Sea. Furthermore, the applied advective pore-water flow pushed the original oxic–anoxic interface down core, thereby increased the advective layer and oxygenated former anoxic sediment layers. The results of the corresponding denitrification measurements (Vistula Estuary, spring) suggested that this oxygenation disturbed the resident microbial community, as the D15 rates (= denitrification of $^{15}N\text{-}NO_3^-$) partly did not increase with increasing $^{15}N\text{-}NO_3^-$ tracer concentrations; in consequence, true denitrification rates (D14, i.e. denitrification of unlabelled NO_3^-) could not be calculated (Nielsen 1992). In the cases where D15 did increase with increasing tracer concentration and thus D14 could be calculated, the resulting rates were very low (Figure 5).

It is likely that the benthic microbial community in the Baltic Sea is not adapted to fast changes between oxic and anoxic conditions such as, for example, observed in the tidal Wadden Sea (North Sea; Marchant et al. 2017), and therefore could not respond to the new position of the oxic–anoxic interface during the incubation time. Consequently, with the advective incubation design used here it was not possible to measure N transformation processes in Baltic Sea permeable sands under realistic pore-water flow conditions (see Sections 4.2.2, 4.2.4).

4.2.2 Nitrogen removal by denitrification

N removal by denitrification and anammox is a natural eutrophication mitigation pathway and was thus investigated at all sites. In all sediment types, denitrification was the only process removing N, which is common in coastal settings likely due to generally high organic matter availability favouring heterotrophic denitrification over autotrophic anammox (Dalsgaard et al. 2005). Based on this assumption, the low organic matter content in the sandy sediments of the Hanko Archipelago and the Vistula Estuary (permeable sand, Table 3) theoretically could have supported anammox. Yet, anammox activity has also been low (Amano et al. 2007, Evrard et al. 2013) or not found (Gihring et al. 2010, Kessler et al. 2012, Marchant et al. 2014, 2016) in other coastal sands, suggesting a more complex control of anammox than just organic matter driven competition.

Denitrification at all sites and in all sediment types proceeded to N_2 as the end product without significant N_2O release. High rates of N_2O release from denitrification have been found in experiments with high DIN enrichment inducing strong organic matter loading (Seitzinger & Nixon 1985) and in subtidal sands (Marchant et al. 2016). Hence, the coastal sandy and muddy sediments of the eutrophic Baltic Sea could theoretically have been a potential source of N_2O. However, none of the investigated sediments was over-enriched with organic matter, as was visible in moderate LOI values (Table 3) and an OPD of several millimetres (Figure 4B), which likely explains the insignificant N_2O release. Denitrification was mainly coupled to nitrification (Dn; Figure 5, black and white bars), which is the common denitrification pathway in coastal sediments with a sufficiently large oxic sediment layer and low NO_3^- concentrations in the bottom water (Rysgaard et al. 1994).

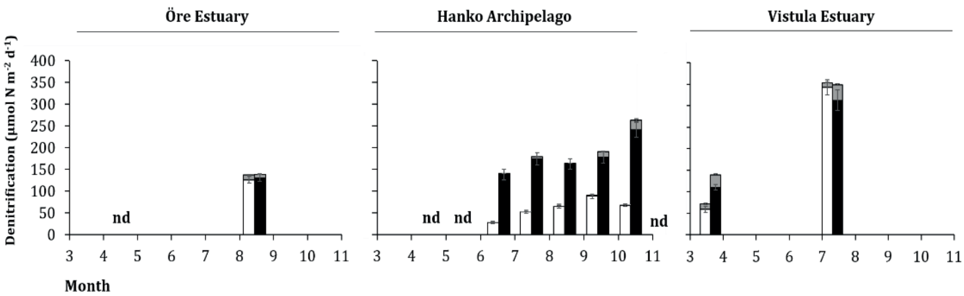

Figure 5: Denitrification rates in the oligotrophic Öre Estuary (ÖE), the eutrophic Hanko Archipelago (HA) and the eutrophic Vistula Estuary (VE), shown for sandy (white bars) and muddy (black bars) sediments, respectively, in the Vistula Estuary for permeable (white bars) and non-permeable (black bars) sandy sediments. Black and white bars give the share of denitrification using nitrate (NO_3^-) from nitrification in the sediment (Dn), and grey bars give the share of denitrification using NO_3^- from the bottom water. Results are shown as averages with standard error. Number of stations included in the average: ÖE: three per sediment type; HA: one per sediment type; VE spring: three of non-permeable sand, two of permeable sand; VE summer: two of non-permeable sand, five of permeable sand; nd = not detectable.

Denitrification in sandy sediments without advective pore-water flow

In the estuaries, denitrification rates were similar in non-permeable sandy and muddy sediments (Öre Estuary), as well as in permeable sands temporarily without advective pore-water flow and non-permeable sandy sediments (Vistula Estuary summer; Figure 5; papers I and II). In contrast, denitrification rates in the Hanko Archipelago were 50–80% lower in the non-permeable sandy sediment than in the muddy sediment (Figure 5; paper III). All sediments experienced the same mass transport (diffusion and fauna-mediated fluxes) and can therefore be expected to have had a similar supply rate of elements into the sediment.

In the estuaries, this was visible in the similar OPD in different sediment types (Figure 4B), indicating a similar depth of the oxic–anoxic interface in the sediment and a similar oxic sediment volume. In consequence, the diffusive path length for denitrification substrates from the bottom water (NO_3^-, labile organic carbon) to the location of denitrification below the oxic–anoxic interface (Christensen et al. 1989), as well as the sediment volume where nitrification can take place, were similar between the sediment types. The different sediment types per estuary had similar concentrations of NO_3^- in the bottom water (papers I and II) and likely a similar availability of labile organic matter as a source of organic carbon and N, due to the homogeneous phytoplankton distribution in the water column and assumed similar bottom currents under seasonal density stratification (paper II). The similar availability and diffusive supply of substrates to both sandy and muddy sediments in each estuary likely resulted in the observed similar denitrification rates.

In contrast, the sandy and muddy sediments in the Hanko Archipelago also had similar NO_3^- concentrations in the bottom water but a likely very different availability of labile organic matter due to the coastal geomorphology. The sandy sediment was located on an exposed transportation bottom, where the bottom flow velocity was high enough to affect the vertical sedimentation of spring bloom phytoplankton. In consequence, part of the phytoplankton can be assumed to have been exported with the bottom water flow, leading to a likely very low residence time and availability of organic matter at the sediment (paper III). Advective intrusion of particles directly into the sediment, as known for permeable sands under high bottom flow (Huettel et al. 1996, Huettel & Rusch 2000), likely did not happen in the non-permeable sand due to the low permeability. Advective pore-water flow and subsequent particle intrusion could only have happened at high bottom flow of > 14 cm s^{-1} over the local sediment topography, which would create pressure gradients high enough to overcome the low sediment permeability (supplementary material paper III). However, such bottom flow velocity was only observed very rarely in winter (0.03% of total measurements, paper III) and therefore not in the measurement period.

Hence, the lower availability of labile organic matter in the non-permeable sandy sediment was the likely reason for the much lower denitrification rates than in the muddy sediment, contrastingly located in an accumulation basin. The potential shoaling of OPD in the sandy sediment (Section 4.1) and the resulting reduced sediment volume for nitrification had likely only a marginal effect on denitrification, which nevertheless was mainly coupled to nitrification in the sediment (Figure 5).

Denitrification in sandy sediments with advective pore-water flow

The Vistula Estuary was the only studied site with permeable sandy sediments and only during sampling in spring could denitrification be measured under advective pore-water flow (Section 4.1). Resulting denitrification rates were about 50% lower than rates measured in the non-permeable sandy sediments of the same estuary and the same season (Figure 5), probably due to problems in the representative simulation of pore-water flow (Section 4.2.1). However, at the time of measurement the estuarine denitrification activity was generally low compared with that in summer, likely due to seasonally low availability of labile organic carbon (see Section 4.2.4). Thus it is unlikely, that the denitrification rates in the permeable sands in spring would have been much higher than the rates in the non-permeable sands of the same season, if obtained under a more realistic simulation of pore-water flow (paper II).

The unexpected environmental conditions encountered in the Vistula Estuary during both sampling campaigns (spring: organic carbon limitation; summer: temporary absence of advective pore-water flow) and the problem of obtaining denitrification rates under realistic advective conditions limit the evaluation of southern Baltic permeable sands as a potentially significant N sink, as previously suggested (Voss et al. 2005, Korth et al. 2013). In theory, the effect of advective pore-water flow on denitrification seems mainly to depend on whether the advective conditions will favour the denitrification of NO_3^- from nitrification in the sediment (Dn) or the denitrification of NO_3^- from the bottom water (Dw), combined with the concentration of NO_3^- in the bottom water. Denitrification rates under advective conditions are commonly assumed to be higher than under diffusive conditions due to a faster supply of substrates. However, if advective pore-water flow favours Dw (Cook et al. 2006, Kessler et al. 2012, 2013) and the concentration of bottom water NO_3^- is ≤ 10 µM, then the supply of NO_3^- to the denitrification layer is low and can reduce total denitrification rates compared with rates under diffusive conditions (Cook et al. 2006). If advective pore-water flow favours Dn (Rao et al. 2008, Marchant et al. 2016), NO_3^- availability from nitrification in the sediment increases with the enlarged oxic sediment volume (Huettel et al. 1998, Marchant et al. 2016), potentially increasing total denitrification rates compared with rates under diffusive conditions.

In the Vistula Estuary, NO_3^- concentrations in the bottom water were < 10 µM in both seasons (paper II), but Dn was the main denitrification pathway, when the permeable sands were incubated with simulated advective pore-water flow (Figure 5). Based on the theoretical considerations above, denitrification rates in the permeable sands of the Vistula Estuary might thus likely be higher under advective than under diffusive conditions. The average denitrification rate during the temporary absence of pore-water flow in summer 2014 was 372 ± 124 µmol N m^{-2} d^{-1}; if the permeable sands had experienced advective pore-water flow within the same season, the denitrification rate could consequently have been > 370 µmol N m^{-2} d^{-1}. Such a change from diffusive to advective conditions could have happened at a bottom flow velocity > 5 cm s^{-1} (calculation based on supplementary material paper II; see also Section 4.1), whereas I cannot evaluate how likely such a flow velocity would be, owing to a lack of published bottom flow data from the Vistula Estuary. If denitrification rates were to double under advective pore-water flow, they would be similar to the lower range of rates measured from the subtidal sandy sediments of the German Bight (870 µM N m^{-2} d^{-1}; Marchant et al. 2016). These considerations are, however, purely theoretical and need more solid data for a realistic estimation of N removal in the permeable sands of the Vistula Estuary.

4.2.3 Availability and residence time of labile particulate organic matter

The coastal denitrification rates in the muddy sediments followed the trophic gradient through the Baltic Sea with highest rates in the eutrophic Vistula Estuary and lowest rates in the oligotrophic Öre Estuary, whereas the denitrification rates in the sandy sediments were lowest in the eutrophic Hanko Archipelago (Figure 5). These results indicate the connection of N cycling to the availability and residence time of labile organic matter within a system (Seitzinger et al. 2006).

The water column at all sites was seasonally density stratified, separating the dissolved elements in surface and bottom water layers. This was particularly obvious in the estuaries, where the riverine freshwater plume had no direct contact with the benthic system. Hence, the riverine dissolved nutrient load could reach the benthic system only after uptake in primary production and subsequent sedimentation of the particulate organic matter (POM) across the stratified water layers (papers I and II). In spring during the time of highest TN load to the estuaries, the water residence time of both estuaries was estimated to be long enough that a high share of riverine DIN could be transformed to phytoplankton POM and vertically exported to the estuarine sediments (papers I and II). Due to the much higher N load (Table 1), primary production in the Vistula Estuary was larger than in the Öre Estuary, resulting in a higher supply of labile POM to the sediment and consequently a higher availability of labile organic carbon and N for benthic N cycling (paper II), also visible in the larger NH_4^+ pool (non-permeable sand, Table 3).

Such tight coupling between pelagic organic matter production and benthic organic matter mineralization as in the estuaries was not visible in the sandy sediment of the eutrophic Hanko Archipelago, where sedimentation of phytoplankton POM was affected by local hydrography (Section 4.2.2). The resulting short residence time of POM was the likely reason for the denitrification rates being lower than in the Öre Estuary, which is oligotrophic, but due to its long particle residence time (≥ 1 year; Brydsten & Jansson 1989) has a high availability of POM. These results emphasize the importance of POM and its residence time for the benthic–pelagic coupling of the stratified coastal zone.

4.2.4 Seasonal variations in nitrogen cycling

The seasonality in N cycling studied in the stratified, aphotic coastal zone was compared with observations from the mixed coastal zone of the Baltic Sea obtained from literature. The depth range (mixed zone < 10 m < stratified zone) was defined based on the average mixed surface layer depth of the Baltic Sea (Leppäranta & Myrberg 2009). While all studied sites were aphotic, the shallower mixed zone is assumed to be mainly photic.

Limited denitrification activity in spring

Independent of sediment type, denitrification activity in spring was low at all sites (Figure 5). This was likely a result of low availability of labile organic carbon in the sediment, as sampling took place before sedimentation of the spring bloom (papers I–III), the annual main source of fresh labile organic matter in the Baltic Sea (Heiskanen & Leppänen 1995). Riverine organic matter load was not considered an important source of labile organic carbon for the studied estuarine sediments in spring: riverine POM was mainly refractory (Öre Estuary) and sank quickly out of the river plume, whereas riverine dissolved organic matter (DOM) was assumed to be mainly confined to the river plume (papers I and II). Similar low denitrification rates in spring have also been found in other Baltic sediments of the stratified, aphotic coastal zone (Hietanen & Kuparinen 2008, Jäntti et al. 2011), but not in shallower, photic sediments. Those sediments likely have sufficient labile organic carbon already in spring, as they receive the main share of land-derived POM and DOM, and additionally often have benthic primary production.

Heterotrophic denitrification uses organic carbon as an electron donor to reduce NO_3^-, in which both substrates are taken up in a 1:1 ratio (Taylor & Townsend 2010), indicating the potential of organic carbon to limit denitrification activity (Slater & Capone 1987, Bradley et al. 1992). In the IPT results, limited denitrification activity was indicated by three observations: labelled N_2 production was close to or below the detection limit, labelled N_2 concentrations did not increase with increasing incubation time, and the D15 rate did not increase with increasing ^{15}N-NO_3^- tracer concentrations, which is one of the main requirements of IPT (Nielsen 1992). All three observations indicate that the ^{15}N-NO_3^- tracer was not consumed by the denitrification bacteria, suggesting a limitation in their metabolism. In such a case, denitrification rates could not be calculated, as observed in the Öre Estuary and Hanko Archipelago in spring (Figure 5). In the Vistula Estuary, denitrification activity was low in spring, but IPT results did not show severe limitation as at the other sites, and rates could thus be calculated. It is likely that the sediments in the Vistula Estuary had received some labile organic matter already before the large spring bloom, potentially from primary production based on the high riverine N load.

As estuaries in the Baltic Sea receive their highest TN load in spring (Table 1), limited denitrification activity in the deeper estuarine sediments in that season seems at first glance like a mismatch in benthic–pelagic coupling. However, due to the density stratification of the water column, riverine N reaches the benthic system only after transformation to phytoplankton POM and subsequent sedimentation (Section 4.2.3), which supplies labile organic carbon and N at the same time to the sediments, enabling denitrification. Hence, the high riverine N load in spring becomes temporary 'trapped' in POM and is eventually removed with a time delay from the riverine peak load (papers I and II). In contrast, a significant part of the spring TN load is probably removed rather promptly in sediments of the shallower, mixed coastal zone. There, sediments are in direct contact with riverine N and are not carbon limited, leading to peak denitrification rates in spring (e.g. Jørgensen & Sørensen 1985, Nielsen et al. 1995, Rysgaard et al. 1995). This implies that estuarine N removal efficiency, i.e. the percentage of N removed from the riverine TN load, should only be calculated in the shallower, mixed coastal zone. In the deeper, stratified coastal zone, the time delay between riverine N load and eventual N removal makes it difficult to say for certain, which riverine load the removed N originated from (paper II).

Seasonal denitrification and DNRA rates

Due to the organic carbon limitation in spring, seasonal heterotrophic denitrification and DNRA rates in sediments of the Hanko Archipelago first became measurable after fresh organic matter input from the spring bloom had reached the sediment. Thereafter, denitrification rates correlated with hydrography-controlled bottom water temperature and peaked in autumn, when the break-up of seasonal density stratification led to highest bottom water temperatures. Denitrification showed the same seasonal pattern in both the studied muddy and sandy sediment, as both were located below the thermocline (Figure 6A). This seasonal pattern of denitrification from the stratified coastal zone contrast the seasonal pattern in the mixed coastal zone, where denitrification rates peak in spring (Jørgensen & Sørensen 1985, Nielsen et al. 1995, Rysgaard et al. 1995). DNRA rates did not show a clear correlation and were likely related to a combination of the factors bottom water temperature, organic carbon to NO_3^- ratio in the sediment and substrate competition with denitrification (Figure 6B). When both processes are heterotrophic, they compete for organic carbon as electron donor, which affects their partitioning: DNRA is favoured at a high organic carbon to NO_3^- ratio, whereas denitrification is favoured at a low organic carbon to NO_3^- ratio (Tiedje 1988, Kraft et al. 2014; paper III).

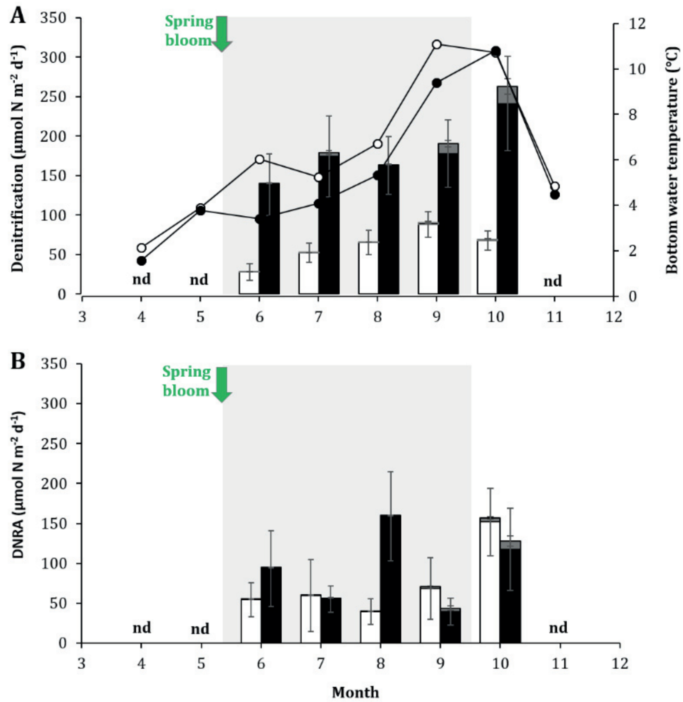

Figure 6: Seasonal rates of denitrification (A) and dissimilatory nitrate reduction to ammonium (DNRA; B) in sandy (white bars) and muddy (black bars) sediment in the Hanko Archipelago, with indicated timing of spring bloom sedimentation and average period of water column density stratification (grey shading). Bottom water temperature is shown for denitrification rates only, due to significant correlation (white circles: sandy site; black circles: muddy site). Black and white bars give the share of denitrification and DNRA using nitrate (NO_3^-) from nitrification in the sediment (Dn, DNRAn), grey bars give the share of denitrification and DNRA using NO_3^- from the bottom water (Dw, DNRAw). Rates are given as averages per sampling month with standard deviation.

4.3 Role of sandy sediments in the aphotic coastal nitrogen filter of the Baltic Sea

The contribution of sand to the aphotic coastal sediments in the Baltic Sea decreases from south to north based on glacial sediment distribution (Al-Hamdani & Reker 2007). The concurrent decrease in sand grain size seems to favour non-permeable sandy sediments at the northern coast (Section 4.1), while they can also be found at the southern coast (Table 3, Forster et al. 2003). Moreover, permeable sands were also found to experience a temporary absence of advective pore-water flow at seasonally very low water energy (Section 4.1). Hence, the characteristics of sandy sediments in the aphotic coastal zone change not only geographically, but also in relation to local and seasonal hydrography.

N removal rates in the studied sandy sediments were affected both by sediment characteristics and local environmental conditions. N removal rates in sandy sediments without advective pore-water flow were similar to rates in other cohesive sediments of the same habitat when also the availability of labile organic matter was similar among the sediments, as seen in the estuaries (Section 4.2.2). This seems also to apply to different habitats of similar organic matter availability, as the denitrification rates in the sandy sediments of the Vistula Estuary in summer (no advection) were similar to the denitrification rates in the muddy sediments of the Himmerfjärden Estuary (northern Baltic Proper; Bonaglia et al. 2014) of the same season, likely due to a similar state of eutrophication. However, when the availability of labile organic matter was different in sandy sediments without advective pore-water flow and other cohesive sediments, the N removal rates were also different, as seen in the Hanko Archipelago (Section 4.2.2). N removal rates in sandy sediments with advective pore-water flow were estimated to be potentially higher than without advective pore-water flow, which theoretically could lead to moderately high N removal rates in the permeable sands of the southern Baltic coast under advective conditions; however, these are only theoretical considerations (Section 4.2.2).

Hence, the studied sandy sediments in the aphotic coastal zone of the Baltic Sea contributed to benthic N removal, independent of whether they were permeable or non-permeable. Process rates were mainly connected to the availability of labile organic matter as a source of labile organic carbon and N. An additional effect of advective pore-water flow on process rates is theoretically possible (Section 4.2.2) but could not be measured. As the availability of labile organic matter differs locally, depending on trophic status, hydrography, geomorphology, as well as water and particle residence time, N removal rates from sandy sediments in the aphotic coastal zone are context dependent and cannot be spatially extrapolated across the diverse Baltic coast.

N retention via DNRA is an important process in the coastal N filter, as it keeps N bioavailable in the sediment and thus can foster eutrophication. However, to my knowledge, the quantification of DNRA in the sandy sediments of the Hanko Archipelago (Figure 6B) presents the first estimate of DNRA in Baltic sandy sediments so far. Strikingly, the average share of DNRA in total NO_3^- reduction was ~ 50%, which was 20% higher than in the muddy sediment and the highest share so far measured in sandy sediments of temperate to cold habitats worldwide. DNRA was likely also the reason for the comparatively large NH_4^+ pool in the organic-poor sandy sediment (Table 3) that could be filled at the average measured DNRA rate (~ 77 µmol N m^{-2} d^{-1}) in only 23 days (paper III).

These results are surprising for two reasons: DNRA in sandy sediments is often considered negligible based on the common environmental conditions in sand expected to disfavour DNRA against denitrification (e.g. low organic carbon to NO_3^- ratio, low concentration of hydrogen sulphide; Tiedje 1988, Kraft et al. 2014), and furthermore, DNRA rates and their corresponding share in total NO_3^- reduction are often very low in cold environments (Giblin et al. 2013). However, in line with my results, there is further emerging evidence that the contribution of DNRA to N cycling both in sandy sediments (Behrendt et al. 2013, Marchant et al. 2014) and cold habitats (Bonaglia et al. 2017) might be currently underestimated. As DNRA was only obtained in the Hanko Archipelago, its rates are, however, not representative of the entire aphotic coastal zone and further measurements are needed to assess its contribution to the coastal N filter.

In summary, the sandy sediments in the stratified, aphotic coastal zone of the Baltic Sea contribute both to removal and retention of N and are therefore an integral part of the aphotic coastal N filter. This applies particularly to the southern Baltic coast, where sand is the main sediment type. Due to the presented environmental context dependency of benthic N cycling, the conclusions drawn for the stratified, aphotic coastal zone cannot be applied to the mixed, photic coastal zone that differs beyond hydrography and light regime also in temperature, seasonality and organic matter availability. For a comprehensive picture of the Baltic coastal N filter, however, N cycling in sandy sediments of both coastal zones should be assessed, particularly as in the shallower zone a higher share of permeable sands and a higher potential for advective N turnover can be expected due to higher water energy.

5 Conclusions and Outlook

The results of this thesis show that sandy sediments in the stratified, aphotic coastal zone of the Baltic Sea contribute significantly to coastal N removal via denitrification and N retention via DNRA and are therefore an important part of the aphotic coastal N filter. Denitrification rates were mainly connected to the availability of labile POM, which functioned as a source of labile organic carbon and N to the aphotic sediments below a density-stratified water column. In response to different availability of labile POM, locally affected by hydrography, geomorphology and trophic status, denitrification rates differed along the Baltic coast. DNRA was quantified for the first time in sandy sediments of the Baltic Sea and had a strikingly high share in total NO_3^- reduction (50%), which could change our current view of coastal sandy sediments. Further studies of DNRA in sandy sediments along the Baltic coast are needed to identify key controls and assess its role in the coastal N filter.

The sandy sediments in the aphotic coastal zone were both permeable and non-permeable, implying the presence and absence of advective pore-water flow. Moreover, during a period of very low water energy, also permeable sands were found to experience an absence of advective pore-water flow. To my knowledge, such a condition in permeable sands has not been described in nature and might be a specific occurrence in the Baltic Sea, favoured by the overall low water energy.

Based on the absence of advective pore-water flow, N cycling processes in non-permeable sandy sediments could be measured with established diffusive incubation methods, which should increase the collection of N cycling data in coastal sandy sediments of the Baltic Sea. In contrast, N cycling processes in the presence of advective pore-water flow could not be measured realistically with the here presented incubation design. An alternative to the challenges and practical limitations of simulating advective pore-water flow in actual samples could be the modelling of N cycling in permeable sands using Multiphysics numerical approaches (Cardenas et al. 2008, Kessler et al. 2015, Marchant et al. 2016). Thereby, bottom water hydrodynamic conditions and bottom topography are used to resolve the pressure field at the sediment surface and the resulting pore-water flow within the sediment (Cardenas & Wilson 2007), which is subsequently coupled to a biogeochemical reactive transport model (Cardenas et al. 2008, Janssen et al. 2012, Kessler et al. 2015). This could be a promising approach to estimate N cycling in the permeable sand of the southern Baltic coast.

All results presented have been obtained from sediments in the seasonally density stratified, aphotic coastal zone, where denitrification followed a different seasonality than in the mixed, photic coastal zone, mainly due to different hydrography. This difference in coastal benthic N cycling needs to be considered in future field and modelling studies. Moreover, the rates and key factors of N cycling from both zones need to be considered for an integrated assessment of the Baltic coastal N filter.

Under ongoing and future climate change, the coastal zone of the Baltic Sea will face a diverse set of environmental pressures that will also affect the coastal N filter. Currently, the most likely scenario includes that the waters of the coastal zone will become warmer, fresher, more strongly density stratified, richer in nutrients, poorer in oxygen and more acidic (BACC II Author Team 2015). Severe oxygen depletion will likely be the key effect on benthic N cycling, as it stops nitrification in the sediment and consequently denitrification coupled to nitrification (Dn; Rysgaard et al. 1994), while it at the same time favours DNRA (Jäntti & Hietanen 2012). Hence, Baltic coastal sediments might remove less, but retain more N leading to an increase in coastal eutrophication (Jäntti & Hietanen 2012). Furthermore, stronger density stratification might also reduce the bottom water flow velocity, as observed in the Vistula Estuary in summer 2014, which would increase particle accumulation in the sandy sediments, reducing their permeability (Forster et al. 2003) and eventually resulting in potentially more non-permeable sands.

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